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SOLUBILITY AND DIFFUSION STUDIES
OF ULTRA PURE TRANSITION ELEMENTS IN
ULTRA PURE ALKALI METALS

FIFTH QUARTERLY REPORT
(June 28, 1964 - October 3, 1964)

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SOLUBILITY AND DIFFUSION STUDIES OF ULTRA
PURE TRANSITION ELEMENTS AND COMPOUNDS IN ULTRA PURE
ALKALI METALS

By R. L. McKisson and R. L. Eichelberger

I. INTRODUCTION

The purposes of this study are: 1) to define the solution process and determine the equilibrium solubility of highly purified transition metals and selected compounds in highly purified liquid alkali metals, and 2) to measure the diffusion of transition metals and constituents of selected compounds in highly purified liquid alkali metals. The material combinations which are to be considered for both the solution and diffusion studies are: iron, niobium, tantalum, molybdenum, tungsten, zirconium, rhenium, vanadium, hafnium, beryllium oxide, niobium monoxide, tantalum monoxide, zirconium dioxide, zirconium carbide, vanadium monoxide, oxygen-saturated zirconium, and oxygen-saturated hafnium with liquid potassium, and niobium and beryllium oxide with liquid lithium. Specific combinations from the above list will be selected, and it is expected that some combinations will not be investigated.

The studies to be made include the measurement of solubility in the alkali metal at temperatures up to 1200°C, coupled with the investigation of the rate-controlling step and its energy of activation; and the measurement of the liquid state diffusion rate and its energy of activation, also to 1200°C.

It is the goal of this study to develop solubility and diffusion data for well-characterized experimental systems, in which the number and range of complicating variables are minimized, in the hope that such data will not only further the understanding of these processes in alkali metal systems, but will also be of use in the materials selection and design of space electrical power system components.

II. SUMMARY

The potassium purification unit has been completed and can be operated with ease. However, the first batch of distilled potassium product analyzed showed a too-high oxygen level for use in the solubility tests.

Modifications of the manipulators have been made to permit a greater range of adjustment on the vacuum seals on the ball and on the sliding joint. These modifications permit the compensation for wear or flowing of the teflon seal in the ball joint, and of the double O-ring seal on the shaft. With these changes, sampling and handling of the potassium can be performed in a vacuum which remains below 1×10^{-6} Torr. Sampling in the low 10^{-6} Torr range is marginally satisfactory, and quite unsatisfactory at 1×10^{-5} Torr.

Single crystal refractory metal crucibles are not yet available. The contractor who is preparing the crucibles by electrochemically machining them from single crystal stock has experienced severe difficulties in adapting his process (which is satisfactory for poly-crystal) to single crystal materials.

The only satisfactory supplier for 1/2" diameter single crystals of refractory metals is MRC. Metals Research, Ltd. has not yet delivered a usable 1/2" diameter single crystal of Nb or Mo.

Analytical methods have now been verified in the 1-10 ppm range for all of the solute materials in potassium. A satisfactory wet chemical analysis for silicon has not been found. For the present silicon will be determined spectroscopically.

III. TECHNICAL PROGRAM

Environmental Test System

The assembly of the potassium purification unit was completed early in July. Following the assembly, several batches of potassium were used in a rinsing operation so that all of the internal surfaces of the components were brought into contact with either liquid potassium or potassium vapor.

The freeze-seals which are used as on-off valves between the components are found to perform very well, and the movement of potassium through the 1/4" O.D. lines is very easily regulated. In general, the transfer of the metal is readily accomplished using rather small helium pressure differentials. Normally, the one and a half psi differential between 26" Hg vacuum and 29" Hg vacuum is adequate to move the liquid potassium. An operating problem was uncovered in that it was difficult to determine when the proper amount of potassium had been transferred into the filter pot from the supply tank. In the original design, three thermocouples of varying length extended into the chamber. The level of the potassium was to have been detected by sensing the temperature changes occurring as the thermocouples became immersed in the rising potassium. In practice, it was easy to detect the presence of hot potassium at the lowest level, but the responses of the intermediate and upper level thermocouples were not adequate to unambiguously indicate the presence of the potassium at these levels. Since these simple thermocouples have proven to be poor liquid level indicators, they were replaced by two thermocouple wells each of which contains a small heater and a thermocouple. The thermocouple is spark-welded to the inner end of the well. When the heater is operating, and the well is not covered with potassium, the poor heat transfer characteristics of the well cause its temperature to rise 20-30°C above the temperature of the surroundings. Then, as the potassium is transferred into the filter chamber and rises to

contact the end of the well, the excess heat is quickly transferred away, and the thermocouple emf drops abruptly. The modified unit now operates very well and gives the required positive response.

In the early testing of the unit, it was convenient to view the inside of the reflux control condenser by looking through the drop counter window through the condenser tube using an ophthalmoscope. In this fashion, condensing potassium could be observed in the reflux control condenser and it was determined that the rates were in general agreement with our expectations from the temperature-levels (vapor pressure-levels) in the distillation column. However, when the temperatures and vapor pressures were high enough to deliver distillate at the desired rate, there was enough streaming of vapor along the condenser tube to slowly cloud and cover the sight glass. Because of the concern that the glass might interact and become an oxygen source in our collected distillate, a baffle was installed to prevent line-of-sight streaming.

After the system was rinsed out following these modifications, a charge of about 200 grams of potassium was distilled into the extruder. The extrusion of the potassium is readily accomplished using 75 foot-pounds of torque on the driving screw when the metal is at 25°C, or using 40 foot-pounds of torque with the potassium at 55°C. The extruded metal is not a cylinder as was desired, but tends to curl quite markedly. Further, the surface of the extruded potassium is very sticky, and it adheres quite tightly to any solid surface so that transferring a solid sample into a vessel is almost impossible. Because of this, a stainless steel transfer funnel has been prepared. The extruded potassium slug will be placed in the heated funnel and the potassium melted to run down the delivery tube into the single crystal crucible. The funnel will be cleaned between loadings, unless several samples are desired in sequence. If this transfer technique proves satisfactory, the stainless steel funnel will be replaced by one made of a more inert material, such as Nb-1Zr.

During the course of these operations, it has been found that in time the manipulators develop leaks in the ball joints, and sometimes in the sliding shaft-seal as well. The problem with the ball-joint appears to be that the original teflon chevron-type seal does not have any provision for adjusting the sealing pressure. A modification in the seal has been made so that the clamping ring can be used to adjust the sealing pressure. A marked reduction of the leak rate during movement of the ball has been noted in the two manipulators which have been modified.

The shaft-seal was also modified so that more pressure can be applied to the double O-ring seal. In the original design an approximately 5 pound force is applied by a spring to deform the O-ring to form the seal. The springs are too weak and do not continue to maintain a tight seal. The springs have been replaced by a sleeve which directly compresses the O-rings. Clamping pressure is developed by using screws which can be tightened as required to effect the desired seal pressure. The changes are shown in Figure 1. Re-work of the remaining manipulators will be deferred until more operating experience is obtained to ensure that these modifications continue to be effective during long term use.

With these modifications, a potassium sample can be prepared and loaded into the transfer vessel in a vacuum of $<2 \times 10^{-6}$ Torr. When this vacuum level is maintained, the sample does not tarnish during the handling procedure. However, in earlier sampling attempts in which the pressure rose to 1×10^{-5} Torr, the potassium developed a pale blue tarnish whose intensity was quite sensitive to pressure, and also to the time of exposure.

Figure 2 shows the sample cut-off operation using the tungsten wire "cheese-cutter." Figure 3 shows the sample in position above the mouth of the transfer vessel. When the tungsten wire is heated the sample, free of any contaminants, drops into the vessel. The vessel is sealed by seating the tapered joint in the cap to that on the vessel. Both photographs were taken through the viewing port when the chamber was under an operating vacuum of 8×10^{-7} Torr.

Material Procurement, Preparation, and Characterization

The single crystal samples of molybdenum, tantalum, and niobium submitted to Sifco Metachemical in Cleveland for electrochemical machining into crucibles have not yet been returned. Sifco is behind schedule on delivery because these single crystal materials behave much differently in their electrochemical process than does polycrystalline stock. They are carrying out a series of modifications of their process in an attempt to develop a satisfactory method, and report in a telephone conversation that they believe that they are close to a solution of the problem. However, if the difficulties in obtaining satisfactory single crystal crucibles cannot be overcome in time for use in the first experiments, high purity zone-refined polycrystalline sample crucibles will be used.

In June, three molybdenum single crystals were received from Metals Research, Ltd. Their specifications called for an 0.45 inch minimum diameter, but the crystals were typically 0.35-0.40 inches in diameter and not usable. A telephone conversation with the MR agent regarding these undersize parts elicited the comment that they observe a decrease in crystal diameter each time they make a zone-refining pass, but the amount of diameter change is very difficult to predict and control. Two of these undersized crystals have been returned.

Recently, three additional molybdenum single crystals were received from Metals Research, Ltd., but they were quite irregular in shape. The diameters ranged from 0.50" to 0.40" along the three-inch length, so that they are not usable.

Two niobium single crystals were received from Metals Research, Ltd. Both were undersize, even though the importance of external size and straightness was previously emphasized to their sales representative in a telephone conversation. The crystals were returned. At present, therefore, we have not received any usable crystals from Metals Research, Ltd.

One 0.45" + diameter, four inch long molybdenum single crystal and one 1/2" diameter, four inch long zone refined polycrystalline iron sample have been received from Materials Research Corporation (MRC). Both samples are usable. One inch will be removed from each for use in making a spot-check of impurity level of these MRC materials.

The technique for electropolishing the inside of the iron crucibles was perfected. An applied voltage of 9 volts and a current range of 20 to 30 amps was used. The principal problem in this study has been to achieve a balance between electrolyte flow and electrode size so that the electrode does not short out to the wall, and does maintain a non-polarizable character. The areas of the polished crucibles were measured by the DLC technique using the standard sample area calibration of 10 $\mu\text{f/sq cm}$ and are shown in Table 1.

Table 1
DLC Measurements on Iron Crucibles

Sample	Geometric Area cm ²	DLC 'Area' cm ²
1	20.6	19.6
2	19.2	20.8

These data indicate that for the electropolished iron crucibles the ratio, DLC Area/Geometric Area, is 1.0, within 8%. This procedure is described by Argue, et al, in "Double Layer Capacitance Measurements on Iron Crucibles to Determine Surface Area," AI-TDR-64-229.

Chemical Analysis

The analytical chemistry support effort requires the determination of the solute metals in potassium at low levels with high precision, and the verification of purity of the solvent potassium and solute metals. During this quarter, the effort has been directed toward the verification of additional analytical methods, the study of analytical procedures for silicon, the analysis of tantalum crucible material, and the analyses of the potassium product for oxygen and sodium. The status of the analytical support program is shown in Tables 4, 5, 6, and 7 in the Appendix.

Methods have now been verified in the 1-10 ppm range for all of the solute materials in potassium. Adequate sensitivity for the determination of sodium in potassium by flame photometry has been demonstrated; 1-50 ppm of sodium in potassium can be determined with a precision of better than ± 0.2 ppm. The accuracy is dependent upon the sodium content of the "standard" potassium and the sodium content of water used as a solvent.

Several approaches to the problem of determining silicon by wet chemistry techniques in niobium, tantalum, and molybdenum have been investigated. None of the state of the art methods tested to date provides adequate sensitivity or accuracy for the determination of silicon in the < 20 ppm range in these metals. For the present, silicon will be determined spectroscopically.

Methods for the determination of niobium and molybdenum in tantalum have been verified and the two MRC tantalum samples on hand have been analyzed. A summary of the results for the analysis of tantalum is shown below.

Table 2
Analyses of Impurities in Single Crystal Tantalum

Impurity	Vendor's Typical Analysis ppm	Chemical Analysis (AI)	
		Ta-1 ppm	Ta-2 ppm
Iron	< 10	10 ± 0.3	6.0 ± 0.3
Molybdenum	< 10	7 ± 0.5	10 ± 0.5
Niobium	< 20	21 ± 0.7	9.2 ± 0.7
Silicon	not reported	Verification of Procedure in progress	

A number of familiarization analyses of oxygen in potassium were made using potassium collected during our purification unit clean-up processing. This material showed oxygen contents ranging up to about 100 ppm, measured by the mercury amalgamation technique on liquid samples pipetted from beneath the surface of the metal. Analyses of

the potassium product collected in the extruder were also made. As is noted above, severe sampling difficulties were encountered and some samples became contaminated during sampling and subsequent handling. Their analyses are, of course, erratic and of little consequence. The analyses of the samples which showed no evidence of tarnishing are shown in Table 3, together with the most recent set of three oxygen analyses of the waste potassium.

Table 3

Determinations of Oxygen in Potassium	
Date of Analysis	Oxygen Content (ppm)
8/24/64 (samples cut from waste K in inert atm. box)	68, 78, 94
9/17/64	40, 36
9/18/64	70
9/29/64	65, 71

The differences in oxygen level between 9/17 and 9/29 cannot be explained, but, in any event, the first batch of collected potassium has a too-high oxygen content for use in the solubility tests. Accordingly, a second batch is being prepared.

The product potassium has been analyzed for sodium with the following result:

- 1) By spectrograph (three samples): <5, 2, and 1 ppm Na
- 2) By absorption spectrophotometry (two samples): 6.4 and 3.1 ppm Na.

The sodium analysis quoted by Mine Safety Appliance Research Corp. for the as-received potassium is 30 ppm Na. It is evident, therefore, that purification with respect to sodium is being achieved in the purification process.

IV. NEXT REPORT PERIOD ACTIVITIES

During the next quarter, the major effort will be directed toward preparing potassium of adequately low oxygen content and toward carrying out experimental measurements on the polycrystalline iron samples; and on the single crystal niobium, molybdenum, and tantalum samples, or, if necessary, on high purity polycrystalline niobium, molybdenum, and tantalum samples.

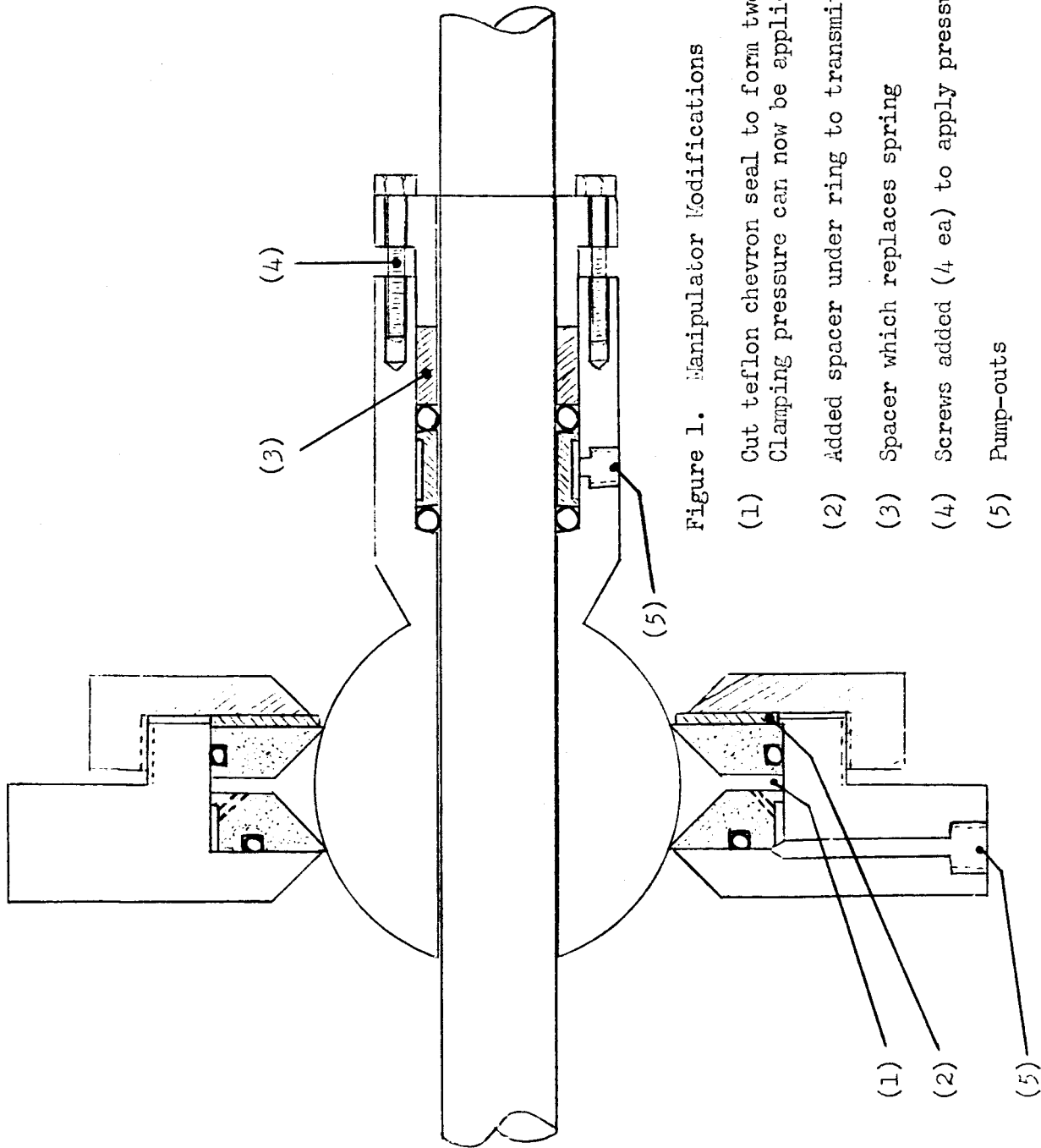


Figure 1. Manipulator Modifications

- (1) Cut teflon chevron seal to form two separate parts.
Clamping pressure can now be applied to teflon lips.
- (2) Added spacer under ring to transmit clamping pressure.
- (3) Spacer which replaces spring
- (4) Screws added (4 ea) to apply pressure to O-rings
- (5) Pump-outs

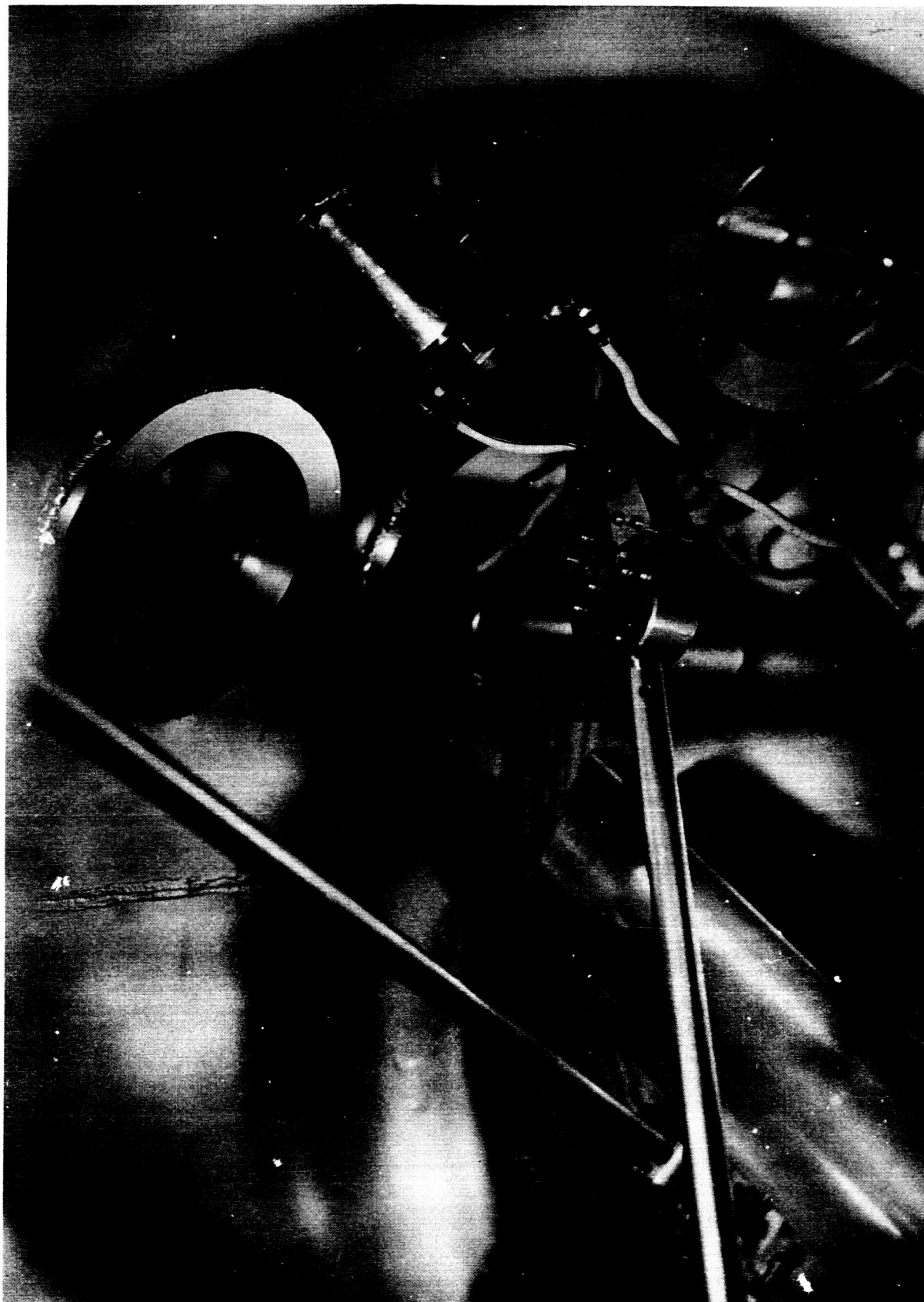


Figure 2. Sample Cutting with the "Cheese-Cutter"

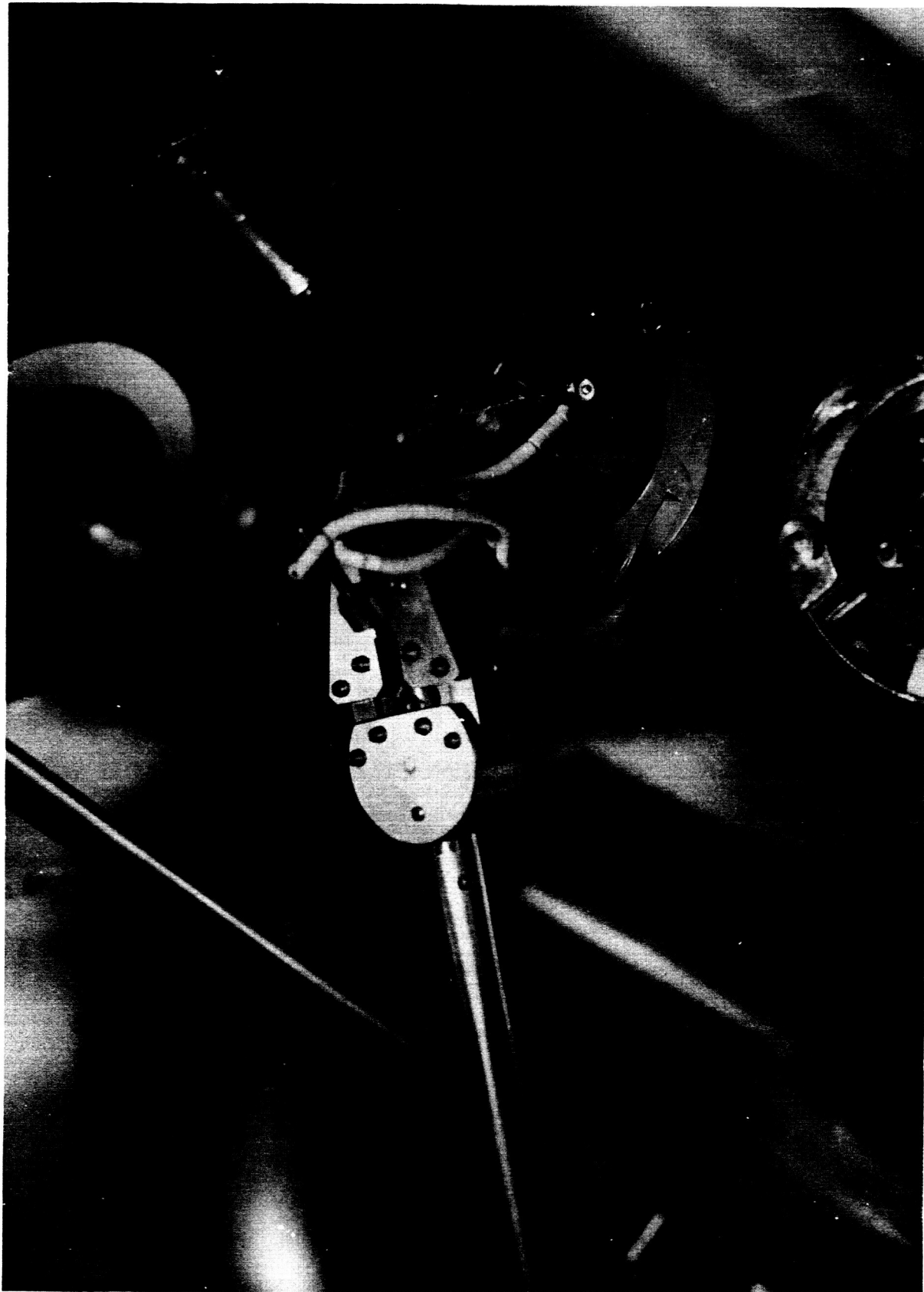


Figure 3. Sample Loading

V. REPORTS ISSUED ON THIS CONTRACT

- R. L. McKisson, R. L. Eichelberger, and J. M. Scarborough,
"Solubility and Diffusion Studies of Ultra Pure Transition
Elements in Ultra Pure Alkali Metals," First Quarterly Report,
AI-9151, November 6, 1963.
- R. L. McKisson, R. L. Eichelberger, and G. R. Argue,
"Solubility and Diffusion Studies in Alkali Metals," Second
Quarterly Report, AI-64-5, February 7, 1964.
- R. L. McKisson, R. L. Eichelberger, G. R. Argue, and J. M. Scarborough,
"Solubility and Diffusion Studies in Alkali Metals," Third
Quarterly Report, NASA-CR-54043 (AI-64-75), May 11, 1964.
- G. R. Argue, W. A. McCollum, and H. L. Recht, "Double Layer Capacitance
Measurements on Ta, Mo, and Nb," AI-TDR-9773, March (1964),
- R. L. McKisson, "Analysis of the Freezing Point Depression Technique
of Determining Impurity Content of Alkali Metal," AI-TDR-9404
(March, 1964).
- G. R. Argue, H. L. Recht, and W. A. McCollum, "Double Layer Capacitance
Measurements on Iron Crucibles to Determine Surface Area,"
AI-TDR-64-229.
- R. L. McKisson, R. L. Eichelberger, G. R. Argue, and J. M. Scarborough,
"Solubility and Diffusion Studies in Alkali Metals," Fourth
Quarterly Report, NASA-CR-54094 (AI-64-156), August 10, 1964.

IV. APPENDIX

TABLE 4

Analytical Method for Determining "Interstitial" Impurities

Element to be Determined	Material to be Analyzed	Method and Description	Sensitivity (a) and Remarks	Ref.	Status of Method
Oxygen	Solute	Micro inert gas fusion or vacuum fusion. Oxygen converted to CO ₂ which will be determined manometrically or by gas chromatography.	No firm limits of sensitivity can be established on the basis of published literature. Possibly a sensitivity in the range of 5-10 micro grams can be achieved. However, equipment and reagent blank corrections lie in this range, making accuracy and precision difficult to maintain. A sensitivity of 0.3 micro gram has been reported. (1)	1,2, 3,4, 5	Since this method is in routine use at AI it was not verified specifically for this project. A lower useful limit of 10 ppm O ₂ has been achieved. Although a precision of ± 1 ppm is observed, the absolute accuracy has not been proved because adequate standards are not available.
Solvent		Mercury amalgamation of the alkali. Oxide residue recovered and titrated with standard acid; or sodium in the oxide residue can be determined by flame photometry. See note (b) regarding oxygen in lithium.	5 ppm \pm 40%, estimate, based on the determination of oxygen in sodium at AI.	6,7. 8,9 10	Equipment and procedure tested, using sodium, at the 15 ppm level. Precision is ± 2.5 μ g. Greater sensitivity is available but there are no adequate standards available to verify the method at lower oxygen levels.
Nitrogen	Solute	Micro Kjeldahl. Nitrogen is converted to ammonia which is determined spectrophotometrically with Nessler's Reagent.	1-2 micro grams	11	The procedure is in routine use at AI and, therefore, not verified specifically for this project.
Solvent		Micro Kjeldahl.	1.0 ppm	12,13	Procedure verified using sodium: Range 1-5 \pm 0.2 ppm.

TABLE 4 (continued)

Hydrogen	Solute	High temperature vacuum extraction of hydrogen which is then determined manometrically or by gas chromatography.	1.0 micro gram	14,15,16,17	Method is used semi-routinely at AI, therefore, verification for this project was not necessary, 1 ppm H ₂ can be determined. Use of mass spectrometer readout is being investigated.
	Solvent	High temperature extraction in iron capsule. Hydrogen diffuses from capsule and is determined manometrically or by gas chromatography.	1.0 ppm	18	Same as above.
Carbon	Solute	Micro combustion to CO ₂ which is determined manometrically or by gas chromatography.	1-10 micro grams. Equipment and reagent blanks limit precision and accuracy.	19,20,21	This technique (utilizing conductometric readout) is used routinely at AI for samples containing more than 50 ppm C. No verification for lower range.
	Solvent	Wet oxidation to CO ₂ which is then determined by gas chromatography.	2 ppm; at this level good accuracy and precision are not expected. No firm data available.	22,23,24	Accuracy and sensitivity limited by reproducibility of the reagent blank which can be determined to a precision of $\pm 5 \mu\text{g}$. No material has been analyzed which contains less than 10 ppm C.
		Dry oxidation.	5-25 micro gram in 0.2 gram sample of Na. 2.0 ± 0.4 micro gram determined in pure Na.	24	Not tested at AI.

TABLE 4 (continued)

Sulfur	Solute	Wet oxidation to sulfate followed by reduction to sulfide which is determined spectrophotometrically with p-amino-dimethylaniline.	1.0 micro gram	25	Method is used at AI on occasional samples. Sensitivity to 1.0 μ g has been demonstrated.
	Solvent	Same as above.	1 ppm	25	Procedure has not been verified in a potassium matrix.
Phosphorous	Solute	Convert to phosphate and determine spectrophotometrically as molybdenum blue.	2 micro grams	26,27	Method is used routinely at AI and, therefore, was not verified for this project.
	Solvent	Same as above.			Verified in a potassium matrix; range 1-10 ppm \pm 5%

NOTES:

(a) Sensitivity is used here to mean the lowest concentration or amount of a substance which can be determined routinely with reasonable accuracy and precision. Except as noted in the Table, data on accuracy and precision which are applicable to the concentration range or to the system of interest are not available in the literature. In these cases, limits of "reasonable" accuracy must be established.

(b) No satisfactory method for determining oxygen in lithium is reported in the literature. The amalgamation method applicable to sodium and potassium is not suitable for the analysis of lithium.⁽¹⁰⁾ The method of Jawcrowski and Potts⁽¹⁰⁾ based on dissolving the alkali in liquid ammonia with the subsequent separation of insoluble oxide is as yet unproved. The best methods reported are those based on activation analysis. According to Bate,⁽²⁸⁾ the fast neutron reaction, $^{6}\text{Li}(n,p)^{6}\text{Li}$ can be used to determine approximately 10 ppm of oxygen, and the reaction, $^{6}\text{Li}(n,\alpha)^{3}\text{He}$, can detect 10^{-3} to 10^{-6} grams of oxygen depending on the beam strength available. An activation method^(28,29) based on the reactions, $^{6}\text{Li}(n,T)^{4}\text{He}$ and $^{6}\text{Li}(T,n)^{4}\text{He}$ should prove especially suitable for the determination of oxygen in lithium. ^{6}Li can be determined by beta counting or gamma counting of the annihilation radiation (^{6}Li decays by positron emission). Sensitivities below 1 ppm might be achieved.

TABLE 5

Analytical Methods Proposed for the Determination of Refractory Solutes in Alkali Metals

Element to be Determined	Method and Description	Sensitivity (in micro grams) and Remarks	Ref.	Status of Method
Iron	Spectrophotometric with o-phenanthroline	0.01-5.0 (\pm 2%)	30,31	Method verified in potassium matrix: 1-10 ppm \pm 2% Alternate method using batho-phenanthroline - 1-10 ppm \pm 2%
Niobium	Spectrophotometric as the reduction product of the complex molybdo-niobate	0.1-10 (above 1 ppm \pm 2%)	32	Method utilizing ammonium thiocyanate as the chromogenic agent was verified in potassium matrix. Range, 1-10 ppm \pm 5%
Tantalum	Spectrophotometric with malachite green	1-2 (to better than \pm 5%; estimate)	33	Method verified in potassium matrix. Range 1-10 \pm 5%
Molybdenum	Spectrophotometric as the thiocyanate, or dithiol complex	1.0 (\pm 2%)	34, 35, 36	Method verified in potassium matrix. Range 1-10 \pm 2%
Tungsten	Spectrophotometric as the dithiol complex	1.0 (to better than \pm 5%; estimate)	36	Method verified in potassium matrix. Range 1-10 \pm 4%
Rhenium	Spectrophotometric as the thiocyanate or for greater sensitivity by the reduction of sodium tellurate under the influence of Re	1.0 (to better than \pm 5%; estimate) 2×10^{-10} g can be detected	37, 38	Method using ammonium thiocyanate as the chromogenic agent was verified in potassium matrix. Range 1-10 \pm 5%
Zirconium	Spectrophotometric with 1-(2-pyridylazo)-2-naphthol (PAN complex)	1.0 (\pm 5%; estimate)	40	Method using pyrocatechol violet verified in potassium matrix. Range 1-20 \pm 5%
Vanadium	Spectrophotometric as the 8-hydroxyquinolate	0.1 (above 1 ppm \pm 2%)	41, 42	Method verified in potassium matrix. Range 1-10 \pm 5%
Hafnium	Spectrophotometric with 1-(2-pyridylazo)-2-naphthol	2.0 (\pm 5%; estimate)	40	Method using pyrocatechol violet was verified in a potassium matrix. Range 2-20 \pm 5%

TABLE 6

Spectroscopic Method for Metallic Impurity Analysis*

Material to be Analyzed	Description of Method	Typical Impurities and Reported Limits of Detection	Ref.	Status**
Potassium and Lithium	Flame Photometry	Other alkali metals can be determined with high accuracy and precision at concentrations near 1 ppm.	43	Atomic absorption spectrophotometry used in place of flame analysis for determination of Na. Method verified in range of 1-50 ppm + 0.2 in KCl matrix. Samples analyzed contained 6.4 and 3.1 ppm Na.
	Emission spectroscopy - Samples converted to sulfate, fused, fined ground, mixed with graphite, d.c. arc, graphite cup.	1 ppm - Mo, Mn, V 1-2 ppm - W, Cr, Ni, Fe 5 ppm - Zn 10 ppm - Ta, Nb	44, 45	Two potassium samples were analyzed. No heavy metals found. Samples converted to chloride. Sodium content was less than 2 ppm. A trace of Ca was indicated but not determined (<5 ppm). (A third sample contained less than 5 ppm Na.)
Iron	Emission Spectroscopy - direct analysis of metal sample using spark technique; or metal sample converted to oxide, mixed with graphite and analyzed.	1-10 ppm - B 10-50 ppm - Al, Co, Cu, Cr, Mn, Mo, Ni, Pb, Si, Sn, Ti, V	46, 47, 48, 49	Samples from polycrystalline iron crucible material analyzed (as metal). Only impurities found were Mg, Si and Mn, all at concentrations of less than 5 ppm.
Niobium and Tantalum	Emission Spectroscopy - sample converted to oxide, Li_2CO_3 used as a buffer, and Ta as internal standard, d.c. arc; or carrier dissolution method, oxide plus Ga_2O_3 .	1 ppm - B 10 ppm - Al, Cd, Cr, Co, Fe, Mn, Mo, Ni, Si, Sn, Ti, Zr 250 ppm - Ta (in Nb)	50 51	Analysis of two samples (oxide form) from tantalum single crystals showed only Fe (<50 ppm), Nb (<100 ppm), and Si (150 + 75 ppm) as impurities. Niobium samples not analyzed.

TABLE 6 (continued)

Molybdenum	Emission Spectroscopy - samples buffered with gra- phite mixtures containing internal standard of Cu or Ni, both high voltage a.c. arc and d.c. arc used.	1 ppm - Ca, Cu, Mg, Mn 4 ppm - Ba, Na 5 ppm - Al, Fe, Si 6 ppm - Cr, Ni 8 ppm - Sn 10 ppm - K, Sr 100 ppm - W	52	Spectrographic analysis (using metal) showed that samples from two single crystals contained only Fe (< 50 ppm) and Si (< 10 ppm) as impurities.
Tungsten	Emission Spectroscopy - carrier distillation, W con- verted to oxide, AgCl used as carrier with Co as in- ternal standard, or with Ga_2O_3 as carrier.	0.5 ppm - Cu, Si 1.0 ppm - Al, Na, Ni 5.0 ppm - Cr, Fe, K, Sn 10 ppm - Mo	51, 52, 53	
Rhenium	Emission Spectroscopy - convert to oxide and utilize carrier distillation; or dissolve in HNO_3 , add car- bon, evaporate, and arc residue.	1 ppm - Bi, Cd, Pb, Sn	54	
Zirconium and Hafnium	Emission Spectroscopy - metal filings or oxides are excited with either a.c. or d.c. arcs, graphite elec- trodes.	Some 22 elements determined at concentrations below 10 ppm with accuracy of $\pm 30\%$	55	
Hafnium in Zirconium	With use of barium fluoride flux	Hafnium to 30 ppm in zir- conium	56	

TABLE 6 (continued)

Zirconium in Hafnium	With use of 12-a, d.c. arc technique	Zirconium to 10 ppm in hafnium	57
Vanadium	Convert to oxide and mix with graphite	1-10 ppm - Al, Bi, Fe, Si, Cd, Mn, Mg, Cu, As, Sb	58, 59

*Spectrographic analyses to be used as a basis for selecting analyses to be performed chemically. See next table.

••Most of the techniques described are used at Al. Verification was limited to materials where actual samples were on hand. The most serious problem encountered is that of pure standards: Materials used on this project are of higher purity than our spectrographic standards, thereby limiting applicability. "Less than" values reported in most cases.

TABLE 7
Colorimetric Analysis of Solute Materials

Matrix Element	Element Determined	Method	Status
Iron	Copper	Biquinoline	Method verified in the range of 1-10 ppm. Sample has not been analyzed due to failure to detect this impurity by spectrographic analysis and a desire to limit expenditures.
	Molybdenum	Thiocyanate	Method has been verified in the range 1-10 ppm \pm 5%. Work on sample discontinued.
	Silicon*		Several methods tested. None satisfactory at concentrations near 10 ppm.
	Manganese	Permanganate	Method verified in range of 1-10 ppm. Sample analyzed and found to contain less than 0.5 ppm Mn.
Niobium	Tantalum	Malachite Green	Work on method discontinued.
	Iron	Ortho-phenanthroline	Method verified in the range 1-10 ppm \pm 5%. Two samples analyzed (11.8 and 11.2 ppm).
	Silicon*	Molybdenum blue	Initial verification work shown to be incorrect. Method is not satisfactory. Work discontinued.
	Iron	Batho-phenanthroline	Method verified in the range of 1-10 ppm \pm 5%. Two samples analyzed. (10.0 \pm 0.3 ppm and 6.0 \pm 0.3 ppm)
Tantalum	Molybdenum	Dithiol	Method verified in the range 3-25 ppm to better than \pm 10%. Two samples analyzed (7.0 \pm 0.5 ppm and 10.0 \pm 0.5 ppm)
	Niobium	Thiocyanate	Method verified in the range of 2-12 ppm \pm 5%. Two samples analyzed. (21.0 \pm 0.7 ppm and 8.2 \pm 0.7 ppm)
	Silicon*		No satisfactory method. Several tested.

TABLE 7 (continued)

Molybdenum	Iron	Batho-phenanthroline	Method verified in the range of 1-10 ppm + 5%. Two samples analyzed (6.0 ± .2 ppm and 5.0 ± .2 ppm)
	Niobium	4-(2-pyridylazo-resorcinol), PAR	Method verified in range of 5-30 ppm ± 5%. No samples analyzed.
	Silicon*		Several methods tested. None satisfactory in range of interest.

*There is a need for research which will provide satisfactory methods for the determination of silicon at levels near 10 ppm.

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